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High Temperature Alkali Corrosion in High Velocity Gases

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HIGH TEMPERATURE ALKALI CORROSION IN HIGH VELOCITY GASES

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ABSTRACT

The effects of potential impurities in coal-derived liquids such as Na, K, Mg, Ca, and Cl on the accelerated corrosion of IN-100, U-700, IN-792, and Mar-M509 were investigated using a Mach 0.3 burner rig for times to 1000 hours in 1-hour cycles. These impurities were injected in combination as aqueous solutions into the combustor of the burner rig. The experimental matrix utilized was designed statistically. The extent of corrosion was determined by metal recession. The metal recession data were fitted by linear regression to a polynomial expression which allows both interpolation and extrapolation of the data. As anticipated, corrosion increased rapidly with Na and K, and a marked maximum in the temperature response was noted for many conditions. In contrast, corrosion decreased somewhat as the Ca, Mg, and Cl contents increased. Extensive corrosion was observed at concentrations of Na and K as low as 0.1 ppm at long times.

INTRODUCTION

One of the major uncertainties in the use of coal-derived liquids to power gas turbines is the effect of residual impurities in such fuels on the life of the hot parts of the turbine. The effects of some of these impurities are known to be adverse. Much work has been done on the effects of impurities such as sodium (Na), potassium (K), and vanadium (V) (see refs. 1 to 5). Such impurities may react with the sulfur in the fuel during the combustion process forming highly corrosive deposits such as sodium and potassium sulfates, sodium vanadates, etc. These corrosive deposits lead to greatly accelerated attack on the hot airfoils of the turbine, resulting in unacceptably short lives. On the other hand, some impurities are known to act as corrosion inhibitors; for example, Ca and Mg (refs. 4 and 5) are often deliberately added to fuels to reduce corrosion. Finally, there are many impurities whose effects are not known and certainly the effects of the interaction of various impurities are largely unknown.

Two potential approaches to determining the effects of such impurities are fruitful. The first is to test many real fuels. By testing a broad spectrum of such fuels, the effects of the various impurities from the analyses of the fuels combusted can be inferred. The main advantage to this approach is that real fuels are burned and that one obtains data under conditions closely approaching those found in a real gas turbine. The main disadvantage of such tests is that the data obtained are relevant only to the fuels actually tested, and usually the range of impurities available is quite limited. Also, currently there are very few liquid coal-derived fuels that are available in quantities sufficient for such tests. The second approach involves the use of clean fuels doped with impurities of interest in a parametric fashion. The advantage of this approach is that such impurity combinations can be carefully controlled and varied in a systematic fashion.

ion. This allows the prediction of attack due to any composition within the range of the impurities studied. The disadvantages to such tests are that they do not burn real fuels under real turbine conditions, and that many tests may be required.

The work described in this report is confined exclusively to the doping approach. The object of this effort is to evaluate the effects of time, temperature and impurity content on corrosion. An earlier report (ref. 6) described such tests. The impurities used in this earlier work were Na, K, Mg, Ca, and Cl, and other variables included in the tests were time, temperature, and fuel-to-air ratio. The temperature range covered in the earlier experiments was from 800° to 1100° C, and the time of the experiments ranged to 200 hours. The concentrations used in these experiments were centered around approximately 0.5 ppm, with variations from 5 to 0.05 ppm, approximately. The parametric additions of the impurities, as well as the other variables, were statistically designed to minimize the number of tests. While weight-change measurements were made, these data cannot be used to satisfactorily evaluate the extent of hot corrosion attack and metal recession measurements (τ) were used in their place. The types of deposits were evaluated by X-ray diffraction.

This work allowed the estimation of attack over a wide range of impurity concentrations at relatively short times; however, the extrapolation of such data to much lower concentrations and much longer times has limited validity. Therefore, the program was extended as described in the current paper to concentrations as low as 0.01 ppm, and to times as long as 1000 hours. Upon the completion of the experiments, most of the data were combined to be evaluated by multiple linear regression into one model. This model can then be used to estimate the effects of these impurities over a broad range of concentrations, temperatures, and times.

MATERIALS

The compositions of the alloys used in this program are listed in table I. The cobalt-base alloy Mar-M509 is a typical vane material which is generally considered to have good hot corrosion resistance due to its high chromium content. The three nickel-base turbine blade alloys cover a range of hot corrosion resistance: IN-792 has moderately good hot corrosion resistance, while U-700 has somewhat poorer hot corrosion resistance, and IN-100 has the least resistance to such attack. All of the alloys were cast by a commercial vendor into the shape shown in figure 1(a). All samples were grit blasted and cleaned with alcohol. Prior to test, each sample was measured along a diameter in the center of the expected hot zone (see fig. 1(a)) with a bench micrometer to a precision of ± 2 micrometers and weighed to ± 0.2 milligram.

PROCEDURE

A burner rig typical of the four used for these tests is shown in figure 1(b) and has been described in reference 7. Briefly, each rig is a nominal Mach 0.3 type fired with Jet A-1 fuel whose sulfur content was determined to be 0.035 ± 0.014 weight percent over the duration of the tests which was approximately 2 years. The fuel-to-air mass ratio was varied from about 0.035 to 0.055. The dopants were injected into the combustion chamber as aqueous solutions. Eight samples were rotated rapidly in front of the exhaust nozzle and reached the desired temperature in a few minutes. After

each 1-hour exposure the burner pivoted away and a forced air cooling nozzle was directed onto the specimens for 3 minutes. Then this cycle was repeated.

At intervals, samples from each alloy were removed and new samples were put in their place. There were several replacement schedules followed during these tests, depending on the total duration of the test. Most of the schedules from the work described in reference 6 resulted in three samples from each alloy at the end of the test: one having been exposed for 40, one for 60, and one for 100 hours. In the later tests, however, where the impurity levels were at their lowest, the samples were scheduled such that at the conclusions of the test specimens were available with exposures of 100, 300, and 400 hours. In a few cases, samples were scheduled resulting in a final evaluation at 100, 400, 500, and 1000 hours.

Regardless of the time of exposure, after each sample was removed from the burner rig it was weighed, washed, and reweighed. Washing consisted of emersion of each sample blade in 300 cm³ of water at 80° C, followed by a soft brushing in running water, an alcohol rinse and air drying. The samples were then sectioned along the plane shown in figure 1(a), which was the center of the hot zone, and where all temperature measurements were made during the run. The cut sections were mounted metallographically, polished and etched. Thickness measurements were made to determine the final thickness at maximum penetration and to calculate maximum metal loss τ , as shown in figure 2. While both the initial and final thicknesses were measured to a precision of ± 2 micrometers, experience has shown (ref. 8) that the resultant change in thickness is only accurate to about ± 20 micrometers at best, and is often as poor as ± 200 micrometers, due to the irregularity of attack and other factors outlined in reference 7. At the conclusion of each test, and before washing, the samples of each alloy exposed for the longest time were scraped and the scrapings were submitted for powder diffraction to analyze the deposits. A few milligrams from each sample were obtained in this fashion and analyzed using a Guinier de Wolf camera. This type of focusing camera was necessary because of the complexity of the patterns of the deposits which resulted in many overlapping diffraction lines in the normal powder camera pattern.

RESULTS AND DISCUSSION

Model Choice and Fitting Procedures

In the preceding report (ref. 6) the data were fitted to:

$$\tau = C_1(\text{Na})C_2(\text{K})C_3(\text{Mg})C_4(\text{Ca})C_5(\text{Cl})t^{B_1} 10^{B_2+B_3T+B_4T^2+E}$$

where each of the functions $C_i(X)$ is of the form

$$C_i(X) = \theta_{i1} + (1 - \theta_{i1}) \exp(-X\theta_{i2}).$$

This particular model had fit the accumulated data about as well as the best fitting second order polynomial approximation, and had a much clearer interpretation. The added data gathered since then have been for considerably lower dopant concentrations and longer time as mentioned previously. Once the new data were included for fitting, making a total of 322 points per alloy, it became apparent that the simpler nonlinear model did not fit as well as the second order polynomial approximation. The model equation was

then modified to fit a polynomial approximating equation using multiple linear regression techniques. This procedure has the advantage that confidence intervals for estimated coefficients and predicted values are more easily determined (refs. 9 and 10).

Table II presents the raw data accumulated throughout the program; included are the X-ray diffraction results. The total range of dopant concentrations are shown schematically in figure 3. The first column of table II provides an identifier for the particular treatment combination, and the second column indicates the rig on which the test was run. The next five columns give the dopant concentrations in ppm, and the eighth column gives the test temperature in degrees C. These data constitute the test conditions. The corrosion products were subjected to X-ray diffraction analysis to identify compounds present. The five columns labeled phase strength provide such X-ray diffraction data as were available. That is, for each compound the strength of observed diffraction lines for any species indicated as being present was designated as weak, medium, strong, or dash for not observed. The next series of columns provide the time for which a specimen was exposed and the corresponding attack, τ . These data except for the 1000-hour values were fitted to a polynomial regression equation using the multiple linear regression analysis techniques as indicated above (refs. 9 and 10). The tentative models chosen were identified partly by using a basic second order polynomial in almost all the variables, that is, time, Na, K, Mg, Ca, Cl, and temperature. The interactions between time and chlorine and temperature were not included in the model because the experiment was somewhat unbalanced with respect to these factors. The 1000-hour data were not included because the combination of long time at very low dopant levels caused these tests to be at the extreme boundaries of the test conditions.

Examination of the data indicated that several three-factor interactions among some of the variables were likely. These were Na-Mg-Ca, K-Mg-Ca, Cl-Mg-Ca, temperature-Mg-Ca, Na-Cl-Mg, and K-Cl-Mg which were included in the model.

Table III presents all the terms of the polynomial considered and the results of the least squares regression. The final model was chosen by examining all the subset regressions using the Mallows Cp statistic as a criterion (ref. 10). Next the value of each estimated coefficient is given with its standard error in parenthesis. It must be pointed out that the scaling indicated in table III was required for each variable in order to achieve a reasonable degree of orthogonality among the terms of the model. Also included in table III are the coefficient of determination (R^2), the mean square error (s^2), the estimate of s , and the number of data points.

The nonlinear model of reference 6 was fitted to these data also, but the lack of its ability to accommodate various interactions caused its fit to be significantly poorer than the polynomial model.

The center point data analysis was presented previously (ref. 6). As mentioned there, the estimate, s^2 , from those data should establish a criterion of comparison because all the variables are held as constant as possible so that the error represents the replication error and does not include any component due to a misspecified model equation. These estimates and estimates from other models are given in table IV.

As shown, the s^2 values using the nonlinear model and all data reported previously for IN-100, U-700, IN-792 are considerably larger than the center point values, while the Mar-M509 is only a little larger. Refitting a smaller data set to the same nonlinear model yields much smaller s^2 val-

ues for all alloys. In fact, only IN-100 remains much larger than the center point estimate. After including the low-dopant long-time data of this report, the nonlinear model turned out to be considerably poorer. The s^2 values listed in table IV for the polynomial models indicate that there is still some serious deficiency with respect to IN-100 (i.e., lack of fit with respect to the model), a less serious deficiency with respect to U-700 and IN-792, and that the s^2 for Mar-M509 is clearly not significantly different than the center point estimate. It is believed (ref. 11) that a large part of the discrepancy is due to the true shape of the τ against time curve that is shown in figure 4. This shape can be only approximated by the necessarily infrequent metal consumption measurements. Thus, using a simple term such as $\log_{10}(\text{time})$ in the model is a serious oversimplification.

Implications of the Model

The models of table III are rather difficult to interpret in any direct examination of terms and coefficients. To facilitate understanding of the resulting equations, a series of parametric plots of attack are shown. Figures 5 to 8 illustrate the property that Na and K induce increased corrosion while Mg and Ca act as inhibitors. In figures 5 and 6, we hold K, Cl, temperature and time at constant values as listed, and plot predicted attack as a function of Na concentration for each of the four alloys. Indications of the reliability of the predictive regression equations are provided by representative two standard error limits on the estimated regression function. In figure 5, Mg and Ca are set at 0.1 ppm. In figure 6, we provide a similar plot of τ against Na, except that Mg and Ca are now at the 1 ppm level. Comparing these two plots shows a general reduction in attack for all alloys for the greater concentrations of Mg and Ca. The reduction is minimal for Mar-M509; it is substantial for IN-100 and U-700. Figures 7 and 8 provide similar plots to indicate the effects of Mg and Ca on K attack. Figure 7 shows the effect of K on attack with Mg and Ca held at 0.1 ppm, while for figure 8 with Mg and Ca set to 1 ppm. Figure 7 shows an increase in attack with K at the lower levels of Mg and Ca, but figure 8 shows little dependence of attack on K. The attack at high levels of K is greatly reduced at the higher levels of Mg and Ca. Figure 9 shows the effect of temperature on attack with all other variables held at their nominal center point values, that is, Na and K at 0.9 ppm, Ca and Mg at 0.47 ppm, Cl at 2.93 ppm, and time held at 100 hours. In general, for all the alloys, there is a maximum in the attack as a function of temperature or such a maximum can be inferred. At times the maximum is either at too low a temperature or too high a temperature to be seen over the range of the test conditions. It is, in general, considered (see ref. 1) to result from hot corrosion being confined to a temperature range in which the corrosive deposits are in their liquid phase. Therefore, at temperatures above the dew point or below the melting point, corrosion should be slight while in the intermediate temperature range, corrosion should be accelerated. However, the fact that the maxima differ with alloy indicates a pronounced alloy chemistry effect.

Figures 10 and 11 are used to illustrate the effects of Cl. In figure 10, Mg, Ca, temperature, and time are held constant with Na and K at 0.1 ppm, while figure 11 is for Na and K held at 1 ppm. These show that increasing Cl decreases attack for both conditions of Na and K. This probably results from the tendency for Cl to decrease the dew points of sodium and potassium sulfates.

One of the most significant interactions indicated in table III is that between temperature and Ca. This interaction is illustrated for each alloy in figures 12 to 15. In each of these figures, Na, K, Mg, Cl, and time are held constant. There are three curves of attack as a function of temperature for three levels of Ca. In figures 12 to 15, there is some indication that the level of Ca affects location of the maximum attack. Higher levels of Ca shift the maximum to higher temperature for the Ni-base alloys IN-100, U-700, and IN-792. However, for Mar-M509, the interaction is seen to be entirely inhibition at low levels of Ca, but accelerating at high Ca levels. As an indication of longer time predictability figures 16(a) and (b) plots the observed and predicted 400 hour data for IN-792 and Mar-M509 respectively. These plots indicate approximately $\pm 2X$ agreement between calculated and predicted values. This agreement seems to hold for U-700, IN-792, and Mar-M509 1000-hour results from LT21 run, but not for the LT22 run. The results are:

	<u>IN-100</u>		<u>U-700</u>		<u>IN-792</u>		<u>Mar-M509</u>	
	LT21	LT22	LT21	LT22	LT21	LT22	LT21	LT22
Observed:	11 431	208	2184	217	1082	297	384	134
Predicted:	3126	1960	2041	1564	793	614	471	445

It should be noted that the LT21 run combines both a very long time and very low dopant concentrations. Likewise the LT22 run combines the most extreme time and lowest concentrations of all dopants.

Deposit Identification

As a result of the many test conditions on the four alloys over the broad range of concentrations in temperature, there is a plethora of X-ray diffraction data. These data are presented in table II. In general, the dopants tended to form the same types of deposits regardless of concentration or the combination with other elements. Mg in the combustion products tended to deposit as MgO. Calcium, on the other hand, reacted with sulfur in the fuel to form primarily CaSO_4 . Both of these phases can be predicted using the chemical equilibrium computer program of Gordon and McBride (ref. 12). This program has been used successfully for such complex systems (refs. 13 and 14). As expected, Na and K also deposited as sulfates. In the case of Na, sodium sulfate was the primary phase; however, it was found in three separate crystallographic modifications (types I, III, and V). K, when present in appreciable quantities, was found as potassium sulfate and also combined with sodium sulfate to form a mixed sodium, potassium sulfate. As noted in the previous work (ref. 6), a phase determined to be Na, K, Ca, Mg sulfate, with the formula $\text{Na}_2\text{K}_2\text{Ca}(\text{SO}_4)_6$, was found for many of the conditions. In a few cases, a sodium calcium sulfate glauberite was found and a few weak lines which were never identified were seen in a few of the patterns. The presence of these phases presented few surprises, as such sulfates formed during reactions have generally been found in these types of tests and usually led to accelerated corrosion (ref. 1). However, because the melting and dew points of several phases, (e.g., $\text{Na}_2\text{K}_2\text{Ca}(\text{SO}_4)_6$), are unknown, the temperature range of maximum corrosive attack can only be estimated.

CONCLUDING REMARKS

An attempt has been made to study the corrosive attack of turbine air-foil alloys as a function of Na, K, Ca, Mg, Cl, temperature, and time utilizing a statistically designed burner rig program. The attack model which was developed from these results seems to account for most of the important first order effects. The model is sufficiently inclusive to allow predictions for concentrations from 0.01 to nearly 10 ppm, and for times from 40 to over 500 hours, and a temperature range of 800° to 1100° C. Most of the first order effects, and a few of the interactions, can be accounted for. The major limitation of the data, and hence the model which is drawn from it, is the inherent inaccuracy of the thickness measurements upon which all of the conclusions are based. A secondary problem is the possibility of a lack of fit in the model. In order for a more precise rendering of attack models with a better definition of the interactions of these attacks to be determined, a more precise method for evaluating the extent of hot corrosion attack must be developed. In spite of these limitations, the level of predictive capability developed here should be sufficient for qualitative estimations of the degree of severity of many future synthetic fuels.

REFERENCES

1. Stringer, J. F., "Hot Corrosion in Gas Turbines," MCIC-72-08, Battelle Columbus Labs., Columbus, Ohio, June 1972.
2. Stringer, J. F., "High Temperature Corrosion of Aerospace Alloys," AGARD-AG-200, Advisory Group for Aerospace Research and Development, Paris, 1975.
3. Lunt, H. E., "Hot Corrosion in Gas Turbines," ASME Paper No. 77-WU/FU-3, Nov. 1977.
4. Lee, S. Y., Young, W. E., and Vermes, G., "Evaluation of Additives for Prevention of High Temperature Corrosion of Superalloys in Gas Turbines," ASME Paper No. 73-GT-1, Apr. 1973.
5. Zetlmeisl, M. J., May, W. R., and Annon, R. R., "Corrosion Inhibitor for Vanadium-Containing Fuels," U.S. Patent 3,926,577, Dec. 1975.
6. Lowell, C. E., Sidik, S. M., and Deadmore, D. L., "Effect of Sodium, Potassium, Magnesium, Calcium and Chlorine on the High Temperature Corrosion of IN-100, U-700, IN-792 and Mar-M509," ASME Paper 80-GT-150, March 1980.
7. Lowell, C. E. and Deadmore, D. L., "Effect of a Chromium-Containing Fuel Additive on Hot Corrosion," Corrosion Science, Vol. 18, 1978, pp. 747-763.
8. Lowell, C. E. and Probst, H. B., "Effects of Composition and Testing Conditions on Oxidation Behavior of Four Cast Commercial Nickel-Base Superalloys," NASA TN D-7705, 1974.
9. Draper, N. R. and Smith, H., Applied Regression Analysis, John Wiley and Sons, Inc., NY, NY, 1966.
10. Neter, J. and Wasserman, W., Applied Linear Statistical Models, 1974, Richard D. Irwin, Inc., Homewood, IL.
11. Deadmore, D. L. and Lowell, C. E., "Nondestructive Evaluation of the Kinetics of High Gas Velocity Hot Corrosion," in preparation.

12. Gordon, S. and McBride, B. J., "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouget Detonations," NASA SP-273, 1971.
13. Material Response From Mach 0.3 Burner Rig Combustion of a Coal-Oil Mixture by G. J. Santoro, F. D. Calfo and F. J. Kohl. NASA TM-81686, December 1980.
14. Deposition and Material Response From Mach 0.3 Burner Rig Combustion of SRC-II Fuels by G. J. Santoro, F. J. Kohl, C. A. Stearns, G. C. Fryburg and J. R. Johnston. NASA TM-81634, October 1980.

TABLE I. - COMPOSITION OF ALLOYS

[All values are weight percent.]

Element	Mar-M509	IN-792	U-700	IN-100
Cr	23	12.7	14.2	10
Ni	10	Balance	Balance	Balance
Co	Balance	9.0	15.5	15
Al	-----	3.2	4.2	5.5
Ti	0.2	4.2	3.3	4.7
Mo	-----	2.0	4.4	3.0
W	7	3.9	-----	-----
Ta	3.5	3.9	-----	-----
Nb	-----	0.9	-----	-----
V	-----	-----	-----	1.0
Mn	-----	-----	<0.01	-----
Fe	-----	-----	0.1	-----
Si	-----	-----	<0.1	-----
Zr	0.5	0.1	<0.01	0.06
B	-----	0.02	0.02	0.014
C	0.6	0.2	0.06	0.18

10

ID	RIG	DOPANT(PPM)					TEMP (C)	PHASE STRENGTH					TIME (HR)	ATTACK(MICROMETERS)			
		NA	K	MG	CA	CL		A	B	C	D	E		IN100	U700	IN792	MM509
CPO	1	0.90	0.90	0.45	0.45	3.21	950	W	-	M	M	S	40 60 80 100	317 554 420 639	294 444 737 708	142 148 161 254	154 73 103 227
CPO	2	0.90	0.90	0.45	0.45	3.21	950	W	-	M	M	S	40 60 80 100	268 328 362 433	359 641 637 757	168 202 172 257	103 125 117 113
CPO	3	0.90	0.90	0.45	0.45	3.21	950	W	-	M	M	S	40 60 80 100	105 224 413 222	113 116 571 132	108 199 141 169	87 76 91 181
CPO	4	0.90	0.90	0.45	0.45	3.21	950	W	-	M	M	S	40 60 80 100	285 359 319 363	433 669 583 594	156 170 118 209	178 98 78 213
BCEFG	1	1.20	1.20	1.00	1.00	5.90	1000	-	-	-	S	S	40 60 100	94 126 258	89 176 291	83 98 133	138 105 166
CDEF	2	0.40	2.00	1.00	1.00	5.90	900	-	-	-	S	S	40 60 100	77 74 67	54 88 69	27 48 62	44 77 130
ACG	3	1.20	1.20	0.20	0.20	3.39	1000	M	W	-	-	-	40 60 100	32 121 140	83 135 150	104 63 124	85 84 206
CDEG	4	0.40	2.00	1.00	0.20	4.49	1000	-	M	-	M	M	40 60 100	97 128 186	98 99 121	85 91 108	126 94 251
ADE	1	1.20	1.20	1.00	0.20	4.99	900	M	M	-	W	S	40 60 100	171 913 1310	95 162 239	61 189 201	58 209 225
ABCD	2	2.00	2.00	0.20	0.20	3.39	900	S	S	W	-	W	40 60 100	764 1299 2490	284 723 1305	180 230 691	205 242 317
BCE	3	1.20	1.20	1.00	0.20	4.49	900	M	W	-	-	S	40 60 100	339 696 1417	39 107 404	103 150 311	124 135 217
CP1	4	0.90	0.90	0.45	0.45	3.21	950	W	-	M	M	S	40 60 100	240 270 548	130 138 491	93 93 173	83 95 154
A=NA ₂ SO ₄ B=K _x NA _{2-x} SO ₄ C=NA ₈ CA K ₂ (SO ₄) ₆ D=CA SO ₄ E=MG0																	

TABLE II. - Continued.

* * * * * *	ID	RIG	DOPANT (PPM)					TEMP (C)	PHASE STRENGTH					TIME (HR)	ATTACK (MICROMETERS)			
			NA	K	MG	CA	CL		A	B	C	D	E		IN100	U700	IN792	MM509
CP2	1		0.90	0.90	0.45	0.45	3.21	950	W	-	M	M	S	40 60 100	376 387 838	278 354 1109	92 134 184	39 135 112
BDG	2		1.20	1.20	0.20	0.20	1.43	1000	S	W	-	W	-	40 60 100	527 540 1102	661 923 1527	380 450 739	189 194 402
ACF	3		1.20	1.20	0.20	1.00	4.80	900	S	-	-	M	M	40 60 100	356 793 1312	68 115 156	75 42 247	36 58 83
BDF	4		1.20	1.20	0.20	1.00	2.84	900	S	-	-	S	S	40 60 100	486 791 1384	110 88 148	62 39 210	64 72 162
FG	1		0.40	0.40	0.20	1.00	2.84	1000	-	-	-	S	S	40 60 100	98 151 203	120 143 236	93 83 157	126 87 93
CP3	2		0.90	0.90	0.45	0.45	3.21	950	W	-	M	M	S	40 60 100	226 244 373	242 403 749	123 116 254	98 116 143
ABEG	3		2.00	0.40	1.00	0.20	4.99	1000	M	-	-	-	S	40 60 100	133 121 132	129 227 217	128 93 199	121 150 169
ABEF	4		2.00	0.40	1.00	1.00	6.41	900	-	-	-	M	S	40 60 100	84 437 839	73 55 79	66 58 70	52 44 96
ABCD FG	1		2.00	2.00	0.20	1.00	4.80	1000	S	-	-	-	-	40 60 100	591 1324 1365	632 994 1495	345 490 1005	127 262 328
(1)	2		0.40	0.40	0.20	0.20	1.43	900	-	M	-	-	S	40 60 100	288 461 233	67 63 106	49 69 207	74 99 134
CP4	3		0.90	0.90	0.45	0.45	3.21	950	W	-	M	M	S	40 60 100	185 156 346	181 87 303	42 96 215	85 117 190
ADEFG	4		1.20	1.20	1.00	1.00	6.41	1000	-	-	-	S	S	40 60 100	144 164 280	146 229 292	108 134 181	94 149 163
BCF	1		1.20	1.20	0.20	1.00	3.57	900	-	W	S	S	S	40 60 100	412 568 1192	136 133 156	66 88 90	98 74 150

A=NA₂ SO₄ B=K_x NA_{2-x} SO₄ C=NA₈ CA K₂(SO₄)₆ D=CA SO₄ E=MGO

1

12

E=MGO

1

1

1

14

A=Na₂ SO₄ B=K_x Na_{2-x} SO₄ C=Na₈ CA K₂(SO₄)₆ D=CA SO₄ E=MGO

TABLE II. - Continued.

ID	RIG	DOPANT (PPM)						TEMP (C)	PHASE STRENGTH						TIME (HR)	ATTACK (MICROMETERS)			
		NA	K	MG	CA	CL			A	B	C	D	E			IN100	U700	IN792	MM509
ACDF	4	1.20	2.00	0.20	1.00	4.80		900	-	-	S	-	S		40 60 100	252 596 1105	132 121 142	73 77 221	45 62 88
C	3	0.40	1.20	0.20	0.20	2.15		900	-	C	M	-	S		40 60 100	449 840 1414	80 93 291	105 235 293	81 166 257
AF	4	1.20	0.40	0.20	1.00	4.08		900	-	-	S	M	M		40 60 100	129 393 1223	70 78 105	58 46 30	43 21 91
BE	3	1.20	0.40	1.00	0.20	3.76		900	S	-	S	-	S		40 60 100	282 530 1545	85 50 109	72 135 241	185 168 219
ABCEF	4	2.00	1.20	1.00	1.00	7.13		900	-	-	S	W	S		40 60 100	88 349 950	53 92 84	54 52 87	66 58 99
ABDFG	3	2.00	1.20	0.20	1.00	4.08		1000	M	-	S	-	-		40 60 100	584 920 1177	636 943 1541	285 334 681	100 132 230
BCDG	4	1.20	2.00	0.20	0.20	2.15		1000	-	S	-	-	W		40 60 100	681 803 1251	412 562 963	331 344 526	119 185 301
CP(ELS)1	4	0.90	0.90	0.45	0.45	3.21		950	W	-	M	M	S		40 60 100	86 248 332	82 144 362	65 52 134	97 120 115
CP(ELS)2	3	0.90	0.90	0.45	0.45	3.21		950	W	-	M	M	S		40 60 100	141 217 304	101 205 230	77 93 114	91 85 191
EXPAND 1	3	0.58	1.23	1.26	0.95	0.46		900	-	W	-	-	M		40 60 100	496 809 1646	82 136 818	59 88 147	73 108 138
EXPAND 3	4	1.50	3.90	1.00	0.75	0.60		900	-	-	-	W	-		40 60 100	872 1413 2677	442 620 1831	244 345 617	271 325 476
EXPAND 5	3	1.90	0.50	1.05	0.79	0.48		900	-	S	-	-	M		40 60 100	541 962 1819	116 203 582	42 66 181	142 133 232
EXPAND 7	4	4.70	1.50	0.83	0.63	0.60		900	-	M	-	-	-		40 60 100	667 1366 1948	228 1077 1952	146 337 759	145 218 299

A=NA₂ SO₄B=K_x NA_{2-x} SO₄C=NA₈ CA K₂(SO₄)₆D=CA SO₄

E=MGO

1

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TABLE II. - Continued.

ID	RIG	DOPANT (PPM)					TEMP (°C)	PHASE STRENGTH					TIME (HR)	ATTACK (MICROMETERS)			
		NA	K	MG	CA	CL		A	B	C	D	E		IN100	U700	IN792	MM509
LT10	4	0.22	0.22	0.14	0.14	0.32	900	-	-	-	-	-	100	725	115	98	134
													300	3129	1892	454	310
													400	4430	2369	1171	248
LT11	3	0.10	0.10	0.10	0.10	0.10	800	-	-	-	-	-	100	443	26	145	39
													300	1313	60	125	163
													400	1184	131	135	262
LT12	4	0.50	0.50	0.10	0.10	0.10	900	-	-	-	-	-	100	1970	472	253	426
													300	5729	2535	1461	619
													400	10382	3739	1567	720
LT13	3	0.10	0.10	0.10	0.10	0.10	900	-	-	-	-	-	100	195	82	149	137
													300	482	89	245	239
													400	1512	243	263	263
LT14	4	0.10	0.50	0.10	0.20	0.10	900	-	-	-	-	-	100	1340	201	220	277
													300	3249	1677	711	320
													400	5681	2575	914	668
LT15	3	0.50	0.10	0.20	0.10	0.10	900	-	M	-	-	S	100	1595	129	145	154
													300	3833	568	994	271
													400	7975	1386	1092	402
LT16	4	0.04	0.90	0.45	0.45	1.00	950	-	-	-	-	S	100	127	105	136	231
													300	212	197	280	210
													400	307	261	252	315
LT17	3	0.10	0.50	0.10	0.10	1.00	900	-	-	-	-	-	100	359	131	59	123
													300	1609	169	137	193
													400	2334	607	189	302
LT18	4	0.10	0.10	0.10	0.10	0.10	1000	-	-	-	-	W	100	147	186	87	128
													300	272	272	224	181
													400	360	392	299	325
LT19	3	0.10	0.10	0.10	0.20	1.00	900	-	-	-	-	S	100	69	55	59	105
													300	99	120	126	118
													400	123	127	128	155
LT20	4	0.50	0.10	0.10	0.20	0.10	900	S	-	-	-	S	100	1546	48	55	165
													300	5522	855	592	301
													400	8409	1763	445	255

A=NA₂ SO₄ B=K_x NA_{2-x} SO₄ C=NA₈ CA K₂(SO₄)₆ D=CA SO₄ E=MGO

TABLE II. - Concluded.

ID	RIG	DOPANT(PPM)					TEMP (C)	PHASE STRENGTH					TIME (HR)	ATTACK(MICROMETERS)			
		NA	K	MG	CA	CL		A	B	C	D	E		IN100	U700	IN792	MM509
LT21	4	0.10	0.10	0.10	0.10	0.10	900	-	-	-	-	-	100	84	30	31	57
													400	1640	511	314	299
													500	4018	985	422	341
													1000*	11431	2184	1082	384
LT22	3	0.04	0.04	0.01	0.01	0.01	900	-	-	-	-	-	100	63	43	39	58
													400	147	71	119	81
													500	108	110	110	105
													1000*	208	217	297	134
LT23	3	0.50	0.10	0.10	0.10	0.10	900	S	-	-	-	-	100	1065	66	110	179
													300	4374	218	463	267
													400	6611	1229	822	431
LT24	4	0.10	0.50	0.10	0.10	0.10	900	-	-	-	-	-	100	826	175	199	206
													300	3921	1791	486	546
													400	5940	2520	1060	605

* Lot included in the final regression analysis.

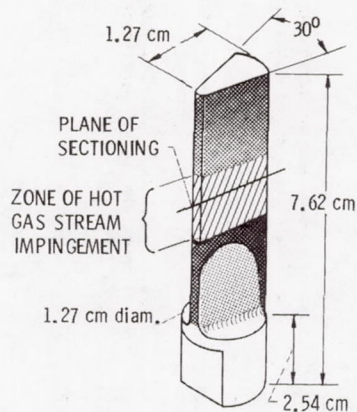
TABLE III. - ESTIMATED REGRESSION COEFFICIENTS FOR THE COMBINED MODEL

(Coefficient estimate (standard error))									The variables in the polynomial equation are defined as:
	IN-100 log (r)		U-700 log (r)		IN-792 log (r)		Mar-M509 log (r)		
Intercept	2.749		2.595		2.316		2.194		τ = attack (microns)
t	1.014	(0.069)	1.142	(0.066)	0.901	(0.046)	0.627	(0.041)	t = log ₁₀ (time (hrs.)/100)
r ₁	-0.053	(0.020)	-0.088	(0.020)	-0.056	(0.014)	0		r_1 = $\begin{cases} -1 & \text{for rigs 1, 2} \\ +1 & \text{for rigs 3, 4} \end{cases}$
r ₂	0		0.047	(0.019)	0		0		r_2 = $\begin{cases} -1 & \text{for rigs 1, 3} \\ +1 & \text{for rigs 2, 4} \end{cases}$
r ₁ r ₂	0.025	(0.016)	0.032	(0.018)	0		0		Na = ppm Sodium -.9
Na	0.644	(0.046)	0.384	(0.046)	0.322	(0.032)	0.191	(0.027)	K = ppm Potassium -.9
K	0.373	(0.042)	0.215	(0.022)	0.279	(0.028)	0.295	(0.025)	Mg = ppm Magnesium -.47
Mg	0.319	(0.089)	0		0		0.198	(0.042)	Ca = ppm Calcium -.47
Ca	0.099	(0.076)	0		0.183	(0.045)	-0.061	(0.034)	Cl = ppm Chlorine -2.93
Cl	-0.249	(0.024)	-0.092	(0.021)	-0.109	(0.015)	-0.126	(0.011)	T = (Temperature (°C) -950)/50
T	-0.152	(0.017)	0.111	(0.017)	0.077	(0.011)	0.052	(0.009)	
Na ²	-0.089	(0.123)	-0.040	(0.013)	-0.028	(0.008)	-0.023	(0.007)	
NaK	-0.120	(0.044)	0		-0.062	(0.031)	-0.088	(0.025)	
K ²	-0.049	(0.011)	0		-0.028	(0.088)	-0.027	(0.007)	
NaMg	-0.284	(0.086)	-0.385	(0.091)	-0.297	(0.060)	0		
KMg	0		-0.281	(0.073)	-0.169	(0.053)	-0.107	(0.046)	
Mg ²	-0.214	(0.040)	-0.281	(0.087)	-0.330	(0.057)	-0.445	(0.059)	
NaCa	-0.203	(0.115)	-0.221	(0.092)	0		0		
KCa	-0.381	(0.094)	-0.187	(0.087)	-0.161	(0.064)	-0.089	(0.050)	
MgCa	-1.321	(0.228)	-0.280	(0.190)	-0.713	(0.131)	-0.333	(0.085)	
Ca ²	-0.718	(0.144)	-0.117	(0.035)	-0.282	(0.073)	0		
NaCl	0		-0.046	(0.015)	-0.047	(0.010)	0		
KCl	0		-0.050	(0.011)	-0.037	(0.008)	-0.016	(0.005)	
MgCl	0		0		0		0.123	(0.018)	
CaCl	(0.361)	(0.074)	0		0.112	(0.036)	0		
Cl ²	0.030	(0.005)	0.035	(0.010)	0.042	(0.006)	0.011	(0.002)	
NaT	0.051	(0.022)	0.057	(0.022)	0.047	(0.015)	0		
KT	0		0		-0.033	(0.017)	0		
MgT	0		0		0		-0.109	(0.027)	
CaT	0.178	(0.052)	0.203	(0.058)	0.298	(0.035)	0.210	(0.029)	
ClT	0		0.018	(0.010)	0		0		
T ²	-0.013	(0.009)	-0.058	(0.010)	-0.019	(0.007)	0		
NaMgCa	0		0		0		-0.363	(0.125)	
KMgCa	0		0		0		0		
ClMgCa	-0.236	(0.112)	-0.144	(0.085)	-0.159	(0.078)	0		
TMgCa	0		-0.293	(0.128)	0		0		
NaClMg	0.097	(0.031)	0.071	(0.039)	0.128	(0.026)	0		
KClMg	0		0.057	(0.031)	0		0		
NaT	0.191	(0.080)	0		0.130	(0.055)	0.098	(0.049)	
Kt	0		0		0		0.109	(0.053)	
Mgt	0		-0.172	(0.139)	-0.249	(0.098)	0		
Cat	0		-0.286	(0.141)	0		-0.399	(0.093)	
S	0.257		0.249		0.170		0.150		
R ²	0.769		0.760		0.819		0.759		
S ²	0.0661		0.0621		0.0290		0.0226		

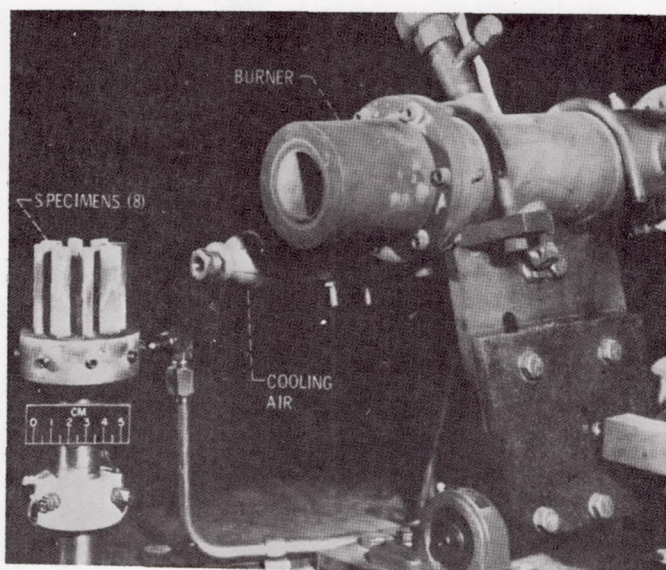
Also given are the coefficient of determination (R^2) and the standard error of estimate (s).

Results Based on n = 322 data points.

Terms were deleted based upon examination of all possible subset regressions using the Mallows C_p criterion.

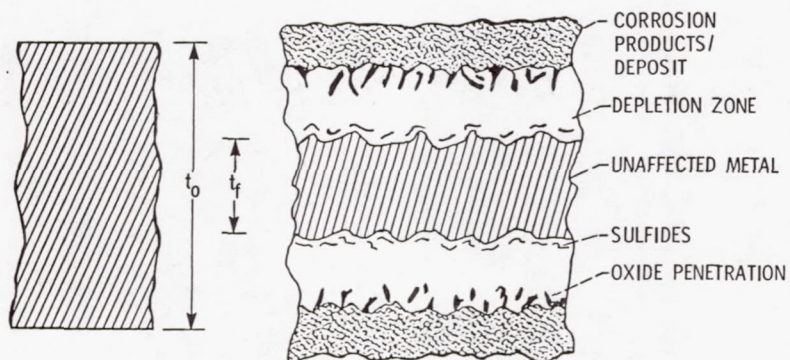


(a) TEST BAR.



(b) BURNER RIG.

Fig. 1 Hot corrosion apparatus and test specimen.



METAL RECESS, $\tau = t_0 - t_f$

Figure 2 - Measurement of extent of corrosion.

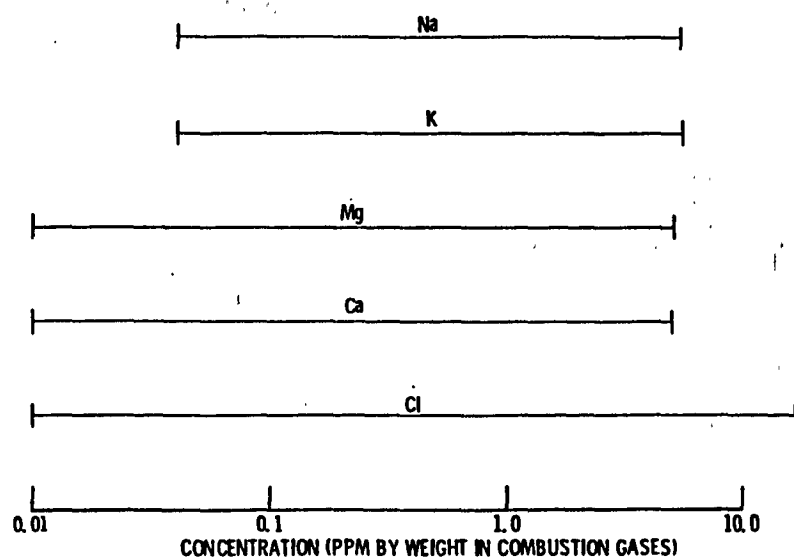


Figure 3. - Impurity range in doped fuel experiment.

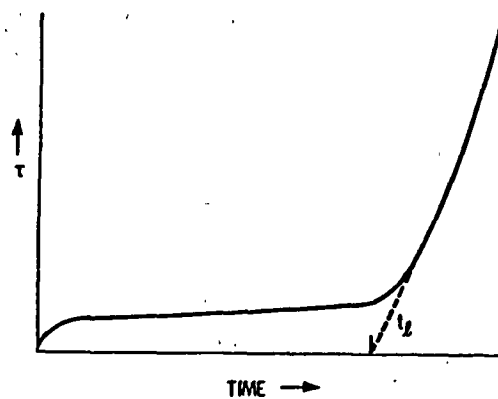


Figure 4. - Hot corrosion kinetics.

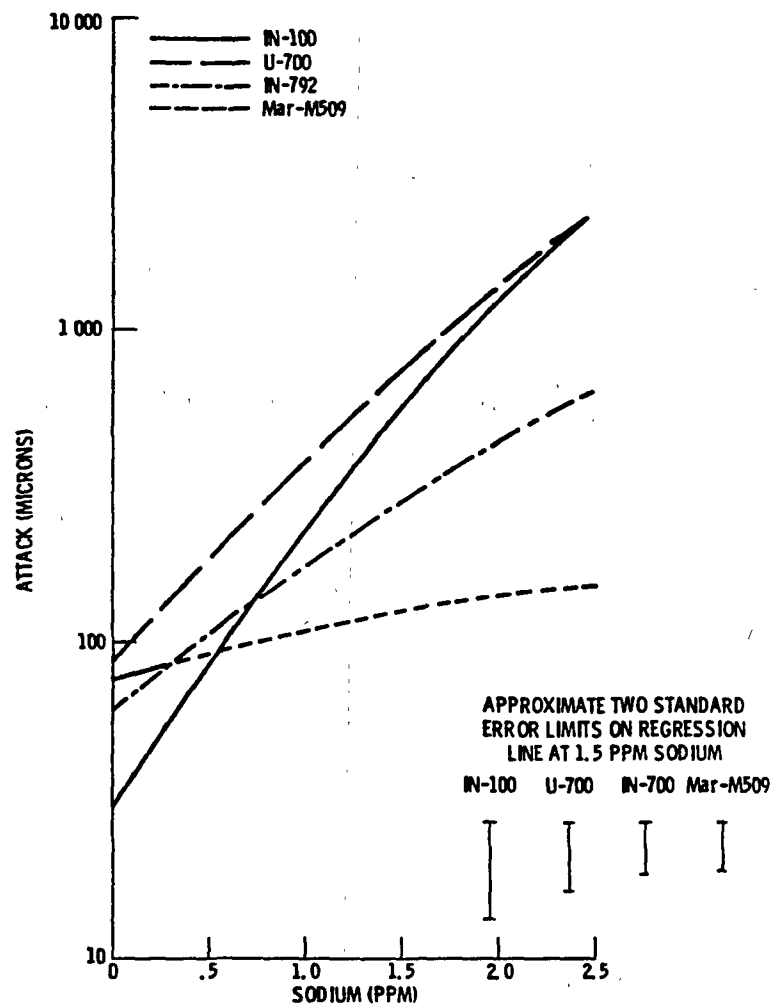


Figure 5. - Attack as a function of sodium with potassium (0.9 PPM), magnesium (0.10 PPM), calcium (0.10 PPM), chlorine (2.93 PPM), temperature (950° C) and time (100 hr) held constant.

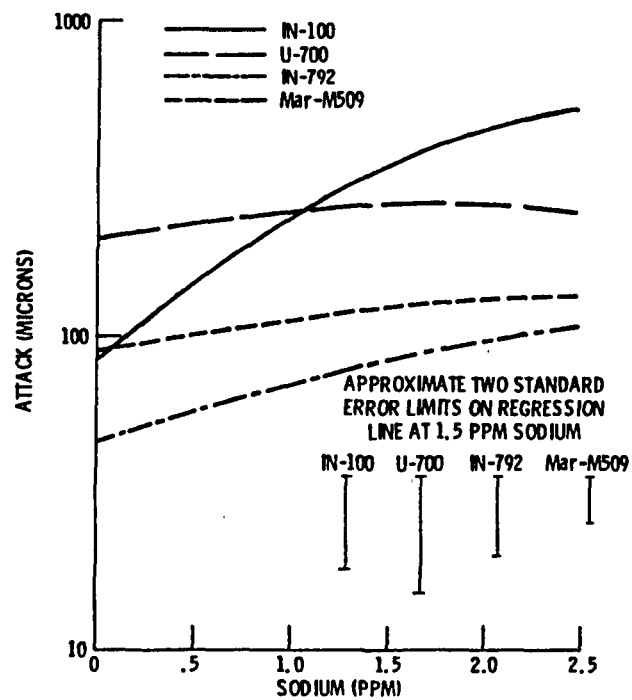


Figure 6. - Attack as a function of sodium with potassium (0.9 PPM), magnesium (1.0 PPM), calcium (1.0 PPM), chlorine (2.93 PPM), temperature (950° C), and time (100 hr) held constant.

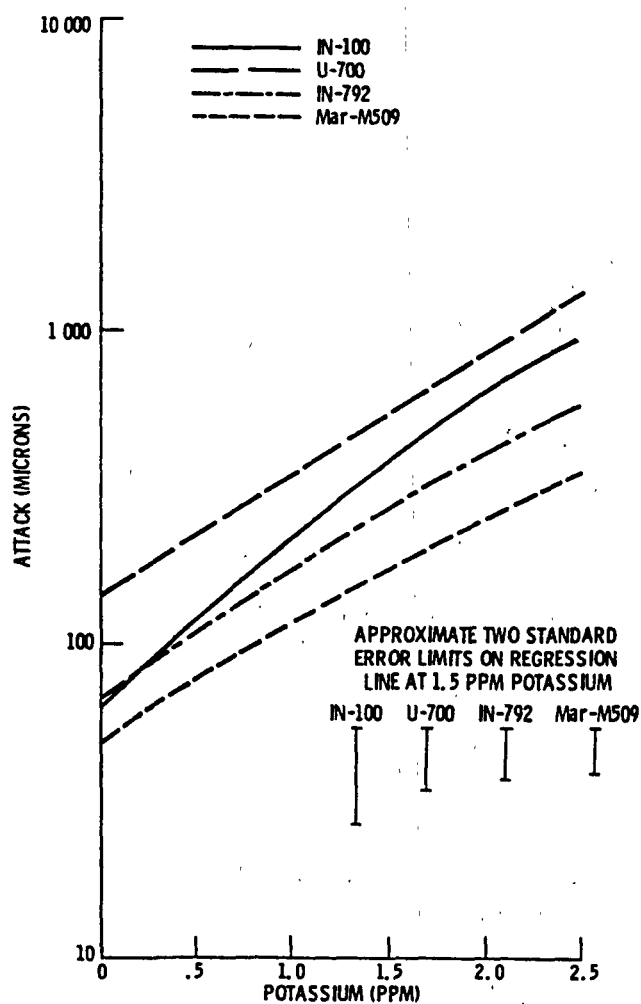


Figure 7. - Attack as a function of potassium with sodium (0.9 PPM), magnesium (0.1 PPM), calcium (0.1 PPM), chlorine (2.93 PPM), temperature (950° C), and time (100 hr) held constant.

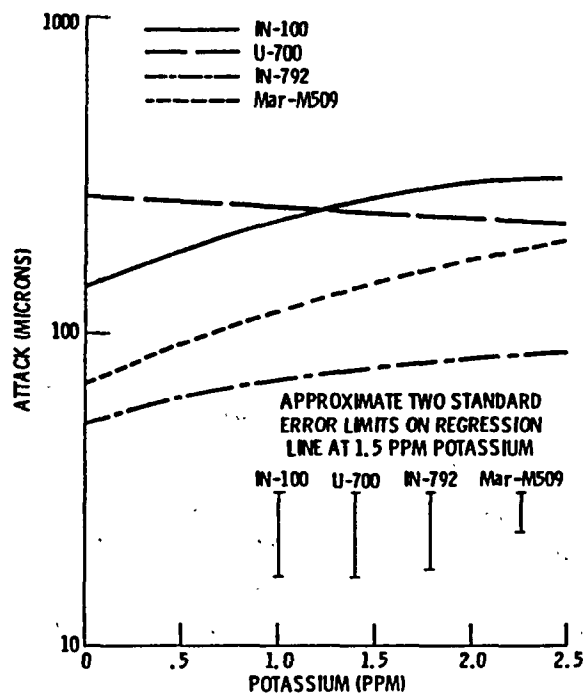


Figure 8. - Attack as a function of potassium with sodium (0.9 PPM), magnesium (1.0 PPM), calcium (1.0 PPM), chlorine (2.93 PPM), temperature (950° C), and time (100 hr) held constant.

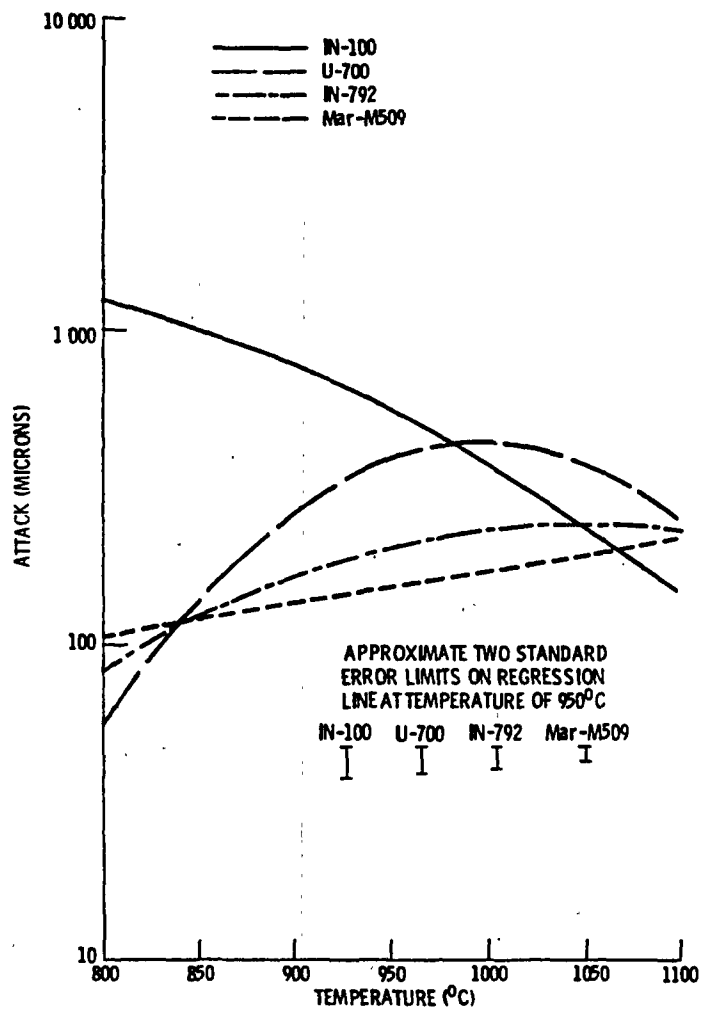


Figure 9. - Attack as a function of temperature with sodium (0.9 PPM), potassium (0.9 PPM), magnesium (0.47 PPM), calcium (0.47), chlorine (2.93 PPM), and time (100 hr) held constant.

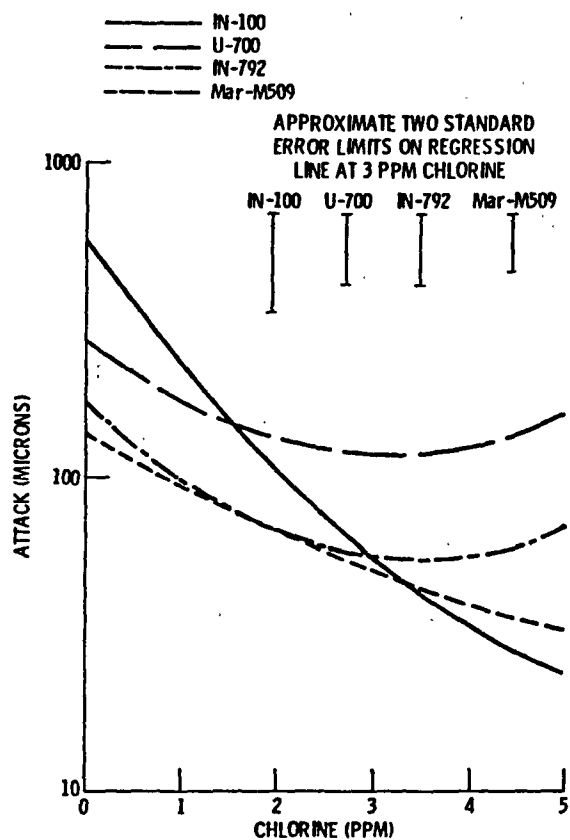


Figure 10. - Attack as a function of chlorine with sodium (0.1 PPM), potassium (0.1 PPM), magnesium (0.47 PPM), calcium (0.47 PPM), temperature (950° C), and time (100 hr) held constant.

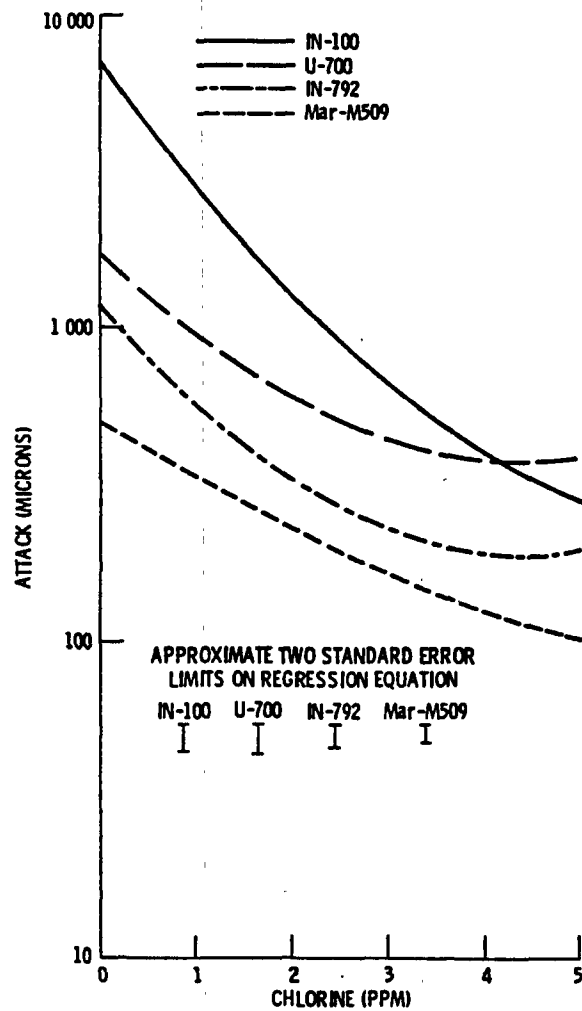


Figure 11. - Attack as a function of chlorine with sodium (1 PPM), potassium (1 PPM), magnesium (0.47 PPM), calcium (0.47 PPM), temperature (950°C), and time (100 hr) held constant.

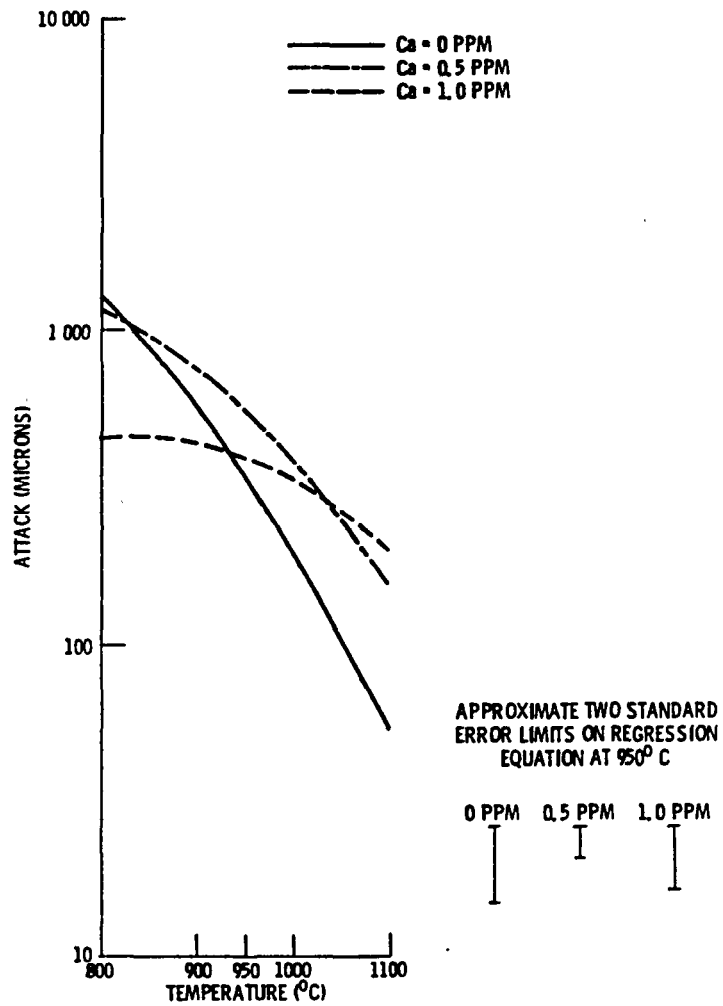


Figure 12. - Attack on IN-100 as a function of temperature at three different calcium concentrations with sodium (0.9 PPM), potassium (0.9 PPM), magnesium (0.47 PPM), chlorine (2.93 PPM), and time (100 hr) held constant.

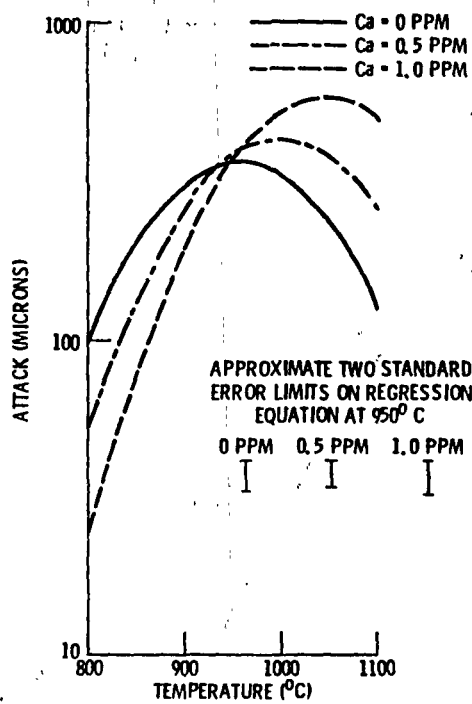


Figure 13. - Attack on U-700 as a function of temperature for the three different calcium concentration; with sodium (0.9 PPM), potassium (0.9 PPM), magnesium (0.47 PPM), chlorine (2.93 PPM), and time (100 hr) held constant.

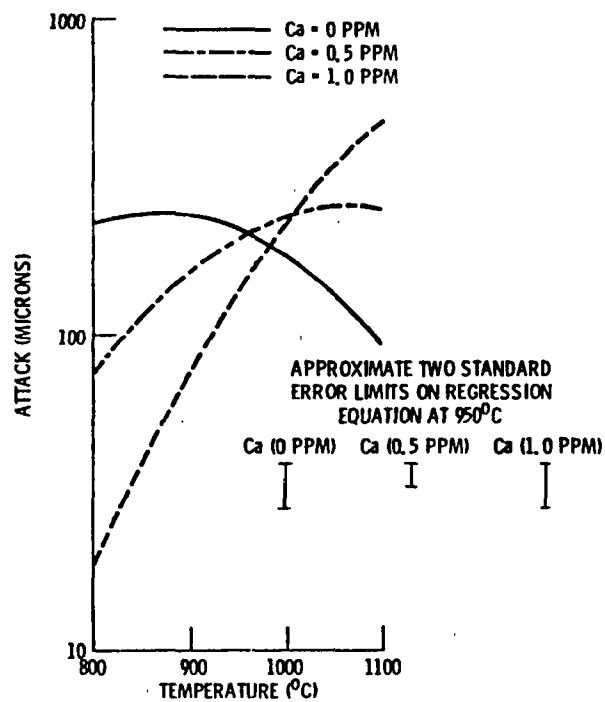


Figure 14. - Attack on IN-792 as a function of temperature for three different calcium concentrations with sodium (0.9 PPM), potassium (0.9 PPM), magnesium (0.47 PPM), chlorine (2.93 PPM), and time (100 hr) held constant.

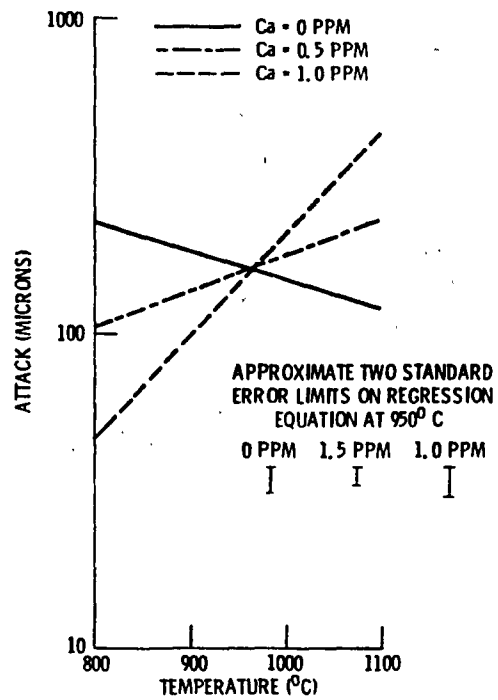
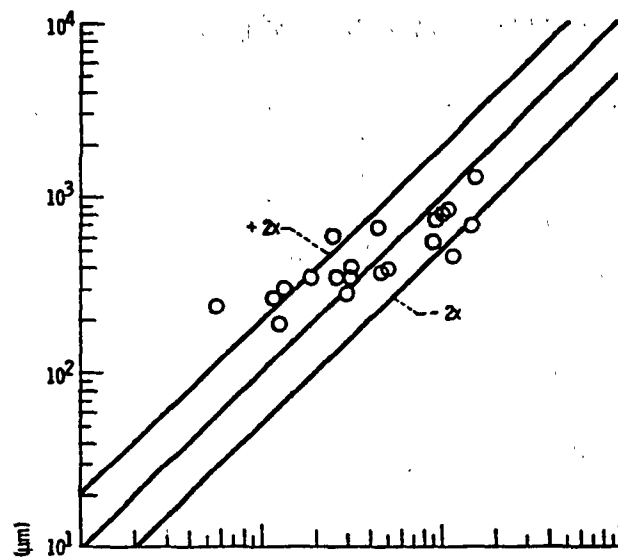
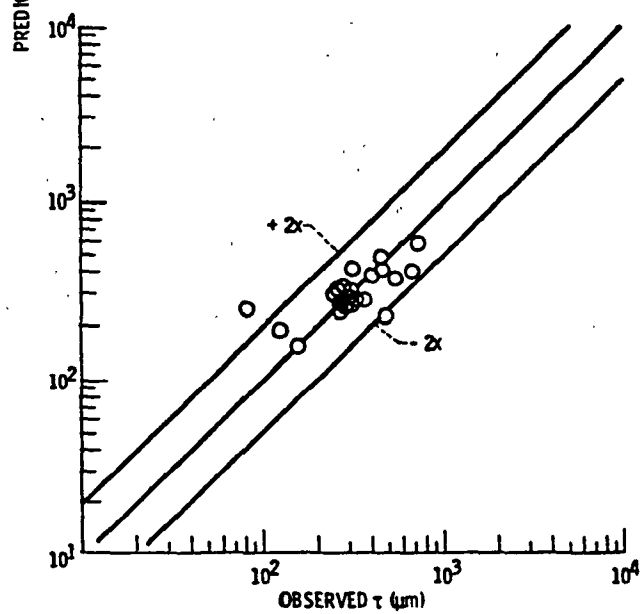


Figure 15. - Attack on Mar-M509 as a function of calcium with sodium (0.9 PPM), potassium (0.9 PPM), magnesium (0.47 PPM), chlorine (2.95 PPM), and time (100 hr) held constant.



(a) IN-792.



(b) Mar-M509

Figure 16. - A comparison of predicted and calculated metal recession values. 400 cycles of one hour at 900°C .

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16. Abstract The effects of potential impurities in coal-derived liquids such as Na, K, Mg, Ca and Cl on the accelerated corrosion of IN-100, U-700, IN-792 and Mar-M509 were investigated using a Mach 0.3 burner rig for times to 1000 hours in one-hour cycles. These impurities were injected in combination as aqueous solutions into the combustor of the burner rig. The experimental matrix utilized was designed statistically. The extent of corrosion was determined by metal recession. The metal recession data were fitted by linear regression to a polynomial expression which allows both interpolation and extrapolation of the data. As anticipated, corrosion increased rapidly with Na and K, and a marked maximum in the temperature response was noted for many conditions. In contrast, corrosion decreased somewhat as the Ca, Mg and Cl contents increased. Extensive corrosion was observed at concentrations of Na and K as low as 0.1 PPM at long times.					
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